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# Thermal modification kinetics and chemistry of poplar wood in dry and saturated steam media

## 1 Introduction

**Abstract:** This research work presents a modelling strategy to analyse thermal conversion rates of two thermal wood modification processes based on time-temperature superposition method. It gathers in a single study different original and bibliographic experimental works analysing the dry mass variation that occurs during thermal and hydro-thermal wood modification processes. The mass loss kinetic was successfully modelled using a modified Arrhenius approach. The time-temperature superposition method allowed to define for each wood modification process a master curve and its time shift depending on the treatment temperature. The analysis of ventilated oven and saturated steam treatments pointed out the existence of a continuous single kinetic for the ventilated oven which became more complex for saturated steam since a second kinetic stage appeared. This kinetic difference was sustained by infrared spectra chemical analysis which showed that hemicelluloses degraded much faster in presence of steam while lignin degradation occurred in both conditions.

**Keywords:** FT-IR chemical analysis; mass loss kinetic; poplar; thermal modification; time-temperature equivalency; wood physical properties.

Thermal (T) and hydro-thermal (HT) modification of wood are widely applied processes which reduces hygroscopicity and enhances dimensional stability, durability and aesthetics. Since HT modification involves a large number of variables many different methods have developed over the years. HT modification can be applied to wood samples with different initial moisture contents, at different temperatures, with different heat diffusion media (CO<sub>2</sub>, N<sub>2</sub>, Air, heating plates, oil, saturated, steam, overheated steam, etc.), at different pressures and with different treatment schedules. The huge number of modification variables together with the large number of wood species available makes the research studies in the field too difficult to compare to one another. A kinetics approach is considered by various authors as one of the best ways to describe T and HT modification processes, either for conventional oven (Goli et al. 2014b; Matsuo et al. 2012, 2016; Marcon et al. 2018) and for saturated steam environment (Endo et al. 2016; Esteves et al. 2007; Navi and Girardet 2000; Obataya et al. 2018). The main physical descriptor of the state of degradation of the sample is recognised to be the dry mass loss as discussed by Candelier et al. (2015, 2016). The kinetics are typically modelled using the time-temperature superposition method and in this paper the method proposed by Goli and Marcon was adopted (Goli et al. 2014b; Marcon et al. 2018). Marcon et al. (2018) modelling approach takes into account a temperature effect on the pre-exponential factor to enhance the predictive ability of the model. A dependency of the pre-exponential factor to relative humidity has also been demonstrated in different scientific studies (Endo et al. 2016; Marcon et al. 2012a, b, c; Obataya et al. 2018).

The chemical analysis of the wood components modifications occurring in the material is a great assessment method to characterise and understand the reactions happening while performing a heat treatment. Those analysis can be driven in different ways, however in the last years vibrational spectroscopies (NIR, FT-IR, Raman), are gaining interest for their simple and fast

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methodology (Reyer et al. 2016; Tondi et al. 2015). A recent article by Hao et al. (2018) focuses on the heat treatment in a furnace under N<sub>2</sub> flux (no presence of oxygen) of poplar (*Populus beijingensis*) at different temperatures (180, 200 and 220 °C). The process was assessed by FT-IR, nutrient content and fungi decay tests. This work shows that cellulose, hemi-cellulose (nutrients) and lignin undergo various degrees of degradation. Moreover, the initial moisture content prior to treatment has a strong effect: the higher the initial MC the higher the nutrient degradation. In the past, the FT-IR has been used to differentiate the so-called natural and artificially ageing methods since the heat treatment is to a certain degree considered a way to accelerate the ageing of cellulosic materials (paper, wood) as in Cocca et al. (2011) and Ganne-Chédeville et al. (2012). In the same way, the FT-IR method will be used to prove ensuing differences between ventilated open air and saturated steam heat treatments in accordance to the mass loss observed.

In order to couple the kinetic studies based on the dry mass loss with the chemical modifications occurring in the cell wall level, several measurements with the well-established ATR FT-IR technology were performed both on T and HT modified samples presenting the same mass losses. The degradation of the wood constituents during T and HT modification of wood is still a controversial argument in wood technology. While it is universally accepted that T and HT modifications affects principally lignin and hemicelluloses, previous studies have shown controversial results as shown in Table 1.

The modification technology involved seems to be an important aspect to be considered and this work aims to compare the effect of two different treatment media such as dry air (ventilated oven) and saturated steam (autoclave) on the same wood species (poplar wood). To achieve this goal a kinetic approach as well as a ATR FT-IR analysis were applied.

## 2 Materials and methods

### 2.1 Wood description

The wood used for this study is Italian poplar (*Populus alba* L.) with a density ( $\rho$ ) of  $340 \pm 2 \text{ kg m}^{-3}$  at standard environmental conditions, 20 °C of temperature ( $T$ ) and 65% of relative humidity ( $RH$ ). The annual ring width was  $10 \pm 2 \text{ mm}$  and the estimated age of the tree is 30 years old. In order to investigate the mass variation due to heat treatments, different types of specimens were cut from heartwood and were described in the following subsections depending on the heat treatment technology performed.

### 2.2 Thermal modification (T) in ventilated oven: sampling and temperatures

The degradation kinetics in ventilated oven was reconstructed from a series of different experiments performed by Goli and Marcon on slightly different sets of samples: a series of samples measuring 30 (L) by 8 (R) by 8 (T) mm<sup>3</sup> and 120 (L) by 20 (R) by 2 (T) mm<sup>3</sup>, were used to perform thermal modifications in the ventilated oven, as described in Goli et al. (2014b) and Marcon et al. (2018) respectively. The specimens were thermally modified starting from the oven dry condition (0% moisture content) reached after at least 48 h exposure at  $103 \pm 2^\circ\text{C}$  in a suitable chamber. The first set of experiments had been conducted in Italy for the temperatures 176, 196, 215, 226, 239, 262 °C; these data were already published by Goli et al. (2014b). The second one had been conducted in Japan for the temperatures of 90, 120, 150 and 180 °C and already published by Marcon et al. (2018). Later on, another set. Both experimental sets were performed using exactly the same poplar board (*Populus Alba* L.). The reference oven dry mass, in order to calculate the dry mass loss ( $\Delta ML$ ), was computed as the difference between the actual dry mass after thermal modification and the reference dry mass before the thermal modification process.

### 2.3 Hydro-thermal modification (HT) in autoclave: sampling and temperatures

The samples used for HT modification measure 30 (L) by 8 (R) by 8 (T) mm<sup>3</sup> and were used to assess the  $\Delta ML$  after saturated steam HT

**Table 1:** Literature review of the main findings concerning wood heat treatments and mass variation.

Authors	Thermal modification technology	Wood species	Lignin	Hemicelluloses
Windeisen et al. (2007)	Dry	Beech	Decompose	Decompose (mostly xylans)
Kocaefe et al. (2008)	Mostly dry	Birch, aspen	Less degraded	More degraded
Brosse et al. (2010)	Dry under N <sub>2</sub>	Beech	Depolymerize/recondensate	Degrades
Li et al. (2005)	High temperature steam	Aspen	–	Hydrolysed and converted in furanics
Yilgor et al. (2001)	Steam	Beech	–	Decreased
Yin et al. (2011)	Steam	Spruce	Degrade/recrosslink	Degrades

modification in an autoclave as in Goli et al. (2014a). Both oven and saturated steam samples were sawn from boards extracted from the same tree. The specimens were oven dried at  $103 \pm 2$  °C before the thermal modification in order to know the oven dry mass. The samples were then equilibrated at standard environmental conditions (20 °C of *T* and 65% of *RH*) and modified in autoclave at the desired temperature and relative saturated steam pressure for the desired time. The samples were modified at the following conditions: 110, 120, 130, 140, 150, 160 and 170 °C at the relative saturated steam pressures. The shortest heating ramp possible was applied in order to get the autoclave to the desired temperature. For 110 °C the heating ramp time was 19 min while for 170 °C the heating ramp time was 74 min. This condition was not avoidable but because most of the treatments were long, the heating time could be neglected. The thermal modification was done on different sets of samples for every condition except the modification at 170 °C where the same set of samples was recursively used. After every cycle the set of samples was oven dried at  $103 \pm 2$  °C and the  $\Delta ML$  determined.

## 2.4 Mass loss kinetic analysis

Kinetics analysis of the dry mass losses during the different thermal modification processes were done according to the method already presented by Goli et al. (2014b). Master curves were identified and the activation energy ( $E_a$ ) determined according to the time-temperature equivalency principle using the Arrhenius theory as in Marcon et al. (2018) taking into account the pre-exponential factor dependency to the treatment temperature. The same data analysis approach was used for all the data set in order to guarantee the results to be comparable. The approximated complex plan (ACP or Cole-Cole plot) was used to check the validity of the time temperature superposition principle (TTSP) and to identify for each treatment a master curve in the same way it was used by Dlouhá et al. (2009) and Peng et al. (2017) to model creep behaviour. This approach was already proved to be efficient for mass variations after oven heat treatment by Goli et al. (2014b). The master curve, identified for a given reference modification temperature chosen arbitrary is described by the three parameters method (rheology like model). The three parameters are: the maximum oven-dry mass loss at infinite modification time ( $ML_\infty$ ), the characteristic time determined at the given reference temperature ( $\tau$ ) and the power parameter that allows to adapt the slope of the curve ( $p$ ). The corresponding kinetic model can be then expressed as in Eq. (1) form:

$$ML_{(t)} = \sum_{i=1}^N ML_{(t \rightarrow \infty)}^i \times \left\{ 1 - \exp \left[ - \left( \frac{t}{\tau^i} \right)^{p^i} \right] \right\} \quad (1)$$

where  $ML_{(t \rightarrow \infty)}$  is the mass loss (%) reached for a theoretical infinite treatment time,  $\tau$  the characteristic time of the considered reaction,  $p$  a parameter that allows to control the slope of the considered reaction kinetic,  $i$  the number of the considered stage, and  $N$  the total number of stages considered for the heat treatment considered.

In this specific case, 150 °C was chosen as reference temperature ( $T_{ref}$ ) for the master curve because it was the only temperature with data from both T and HT modification. Afterward, the TTSP was performed by shifting all experimental data toward the reference temperature and identifying the activation energies ( $E_a$ ) involved in each processes allowing for comparison between the two processes performed for the present study with different technologies and treatment media (air or steam).

Studies by Altgen et al. (2020) have shown that a leaching process can remove the residues produced during the thermal treatment under dry or pressurized hot water conditions. One main consequence of no leaching of the samples was the eventual underestimation of the real mass loss if ones aim to compare results under such peculiar conditions. However, in the present work, no leaching was performed to ensure that the results were comparable with most of the available literature among which the experimental data base and its analytical conversion rate modelling from Marcon et al. (2018). This guarantee too that the outcomes are directly transferrable to industries where the leaching was not foreseen.

## 2.5 Cell wall chemical modification

Samples displaying the same mass variations from both modification processes up to a dry mass loss around 9% were analysed to assess the chemical modifications occurring during each step within the same modification technology and for the sake of comparison between those two technologies. Since the temperature of 150 °C was the only temperature where the temperatures used for T and HT modifications overlapped up to a reasonable mass loss, the samples modified at this temperature were chosen to perform the FT-IR analysis. The FT-IR analysis was performed on samples with dry mass losses of 3.55% (166 h of oven), 8.81% (411 h of oven) and 11.30 % (600 h of oven) for T modification, and for dry mass losses of 2.5% (1 h of autoclave), 4.06% (2.5 h of autoclave), 9.01% (5 h of autoclave) for saturated steam. Thin slices of around  $5 \times 3 \times 1$  mm<sup>3</sup> were cut from the specimens once stabilized at standard environmental conditions (20 °C and 65% *RH*) and undergone to ATR FT-IR analysis with a PerkinElmer Frontier instrument equipped with an ATR-Miracle diamond crystal. The slices were laid on the diamond eye (1.8 mm diameter) of the ATR equipment and the contact was ensured by tightly screwing the clamp device. Each sample was scanned in triplicate registering the spectrum with 32 scans at a resolution of 4 cm<sup>-1</sup> in the wave number range between 4000 and 600 cm<sup>-1</sup>. The average of these spectra after unit vector normalization and standard baseline correction performed with Unscrambler software by Camo Analytics (Oslo, Norway) was compared in the fingerprint region between 1800 and 600 cm<sup>-1</sup> more likely to exhibit variation since related to the chemical composition of the cellulose, hemicellulose and lignin (Schnabel et al. 2014).

The implementation of the leaching procedure presented by Altgen et al. (2020) before the FT-IR analysis could have led to slightly different results by removing the degraded parts of hemicelluloses present inside the cell wall. But, as already mentioned in the previous subsection, it was chosen to compare the different processes without leaching since conventional processes do not involve water in its liquid form which could leach the products.

# 3 Results

## 3.1 Mass variation kinetics

The dry mass loss during modification in ventilated oven and under saturated steam versus the logarithm of the modification time is shown in Figure 1. As it can be observed and commonly found in literature, the process

was much faster under saturated steam atmosphere than in dry air oven. For instance, under saturated steam conditions 50 h of treatment at 150 °C corresponds to a dry mass loss of 20% while for ventilated oven the mass loss at the same temperature and modification time was only 4%. The same 20% of  $\Delta ML$  in the ventilated oven at 150 °C was reached after about 1500 h of treatment. Saturated steam showed to be much more effective than ventilated oven. Both ventilated oven and saturated steam mass loss kinetics seemed to be easily predictable with a kinetic model.

Both those experimental results were in line with the previous studies stating that the T and HT modifications, at least for reasonable temperatures (<250 °C), were displaying a time temperature equivalency feature. The same model than in Goli et al. (2014b) and Marcon et al. (2018), based on the modified Arrhenius law and time temperature superposition method, could be applied to define with few parameters the kinetics of both processes and ease their understanding.

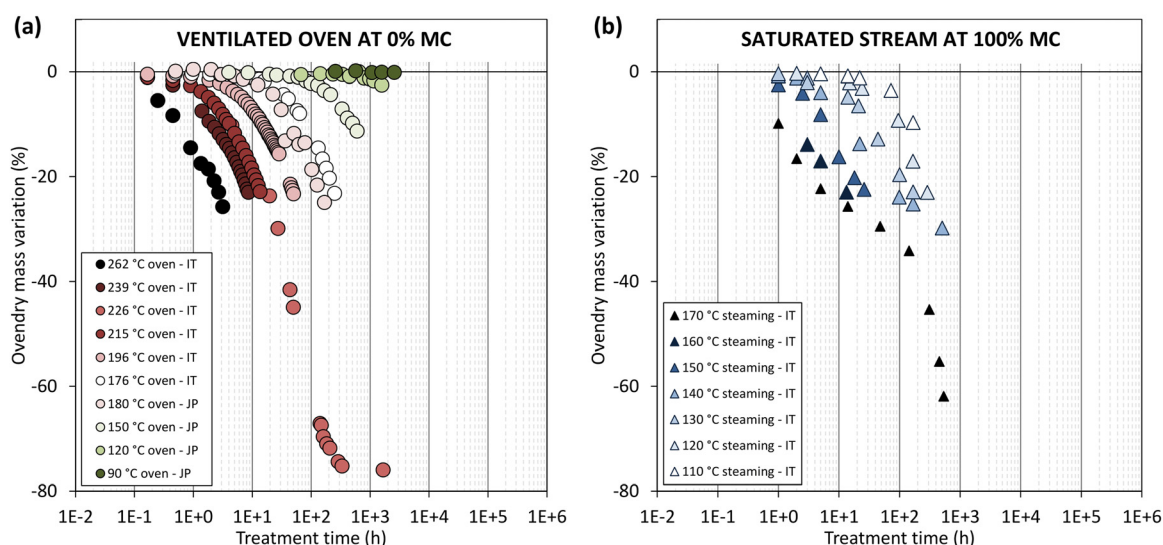
### 3.2 Master curves: time-temperature superposition method

Experimental data were modelled with master curves at the chosen reference temperature of 150 °C by time shifting the experimental points at other temperature to that reference one as in Figure 2. The ACP (or Cole-Cole plot) discarded the time variation from the different temperatures and allowed to identify the master curves coefficients summarized in

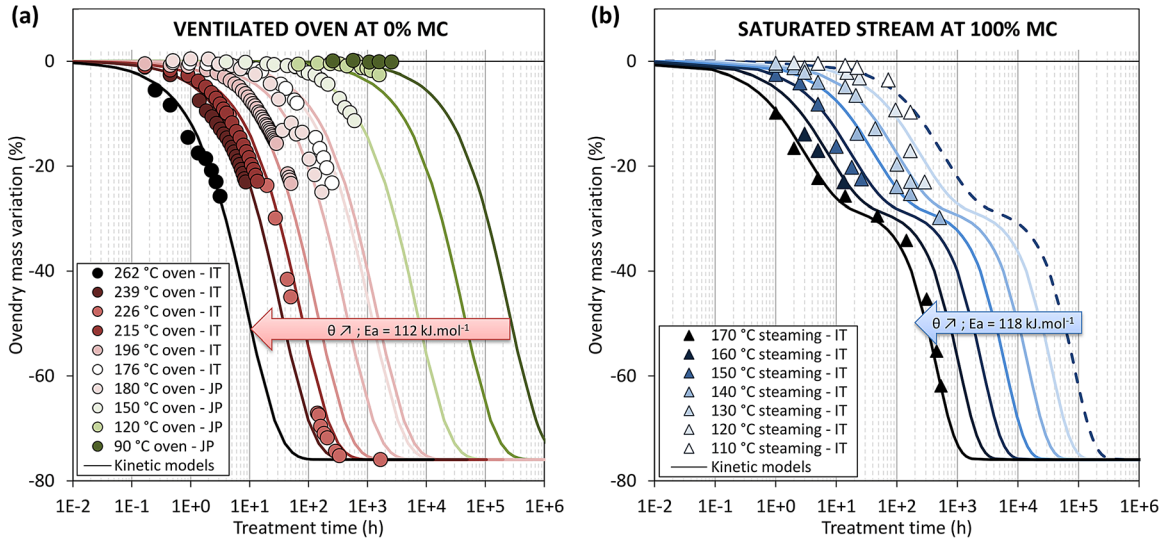
Table 2 from Eq. (1). For the sake of brevity, the whole details of the TTSP application were not provided.

Master curves were plotted in a sole graph in Figure 2 which showed how the master curves of the two modification processes were rather different both in time and shape. Mainly, the master curve of the saturated steaming showed an inflection point at around 28%  $\Delta ML$  where the kinetics slows down. This phenomenon led to consider a master curve with two stages for the saturated steam where one or more characteristic reaction can act separately or superpose. As said before, the master curves descriptors are reported in Table 2.

As shown in Table 2, the beginning of the degradation reactions was very different between T and HT and within the same reaction as for the HT modification. Indeed, ventilated oven exhibited a single stage modification kinetic with a time constant ( $\tau$ ) of 7000 h. Saturated steam modification showed a two stage reaction: one possibly depending mainly on the thermal degradation of polymers and the other mainly on the interaction of polymers with temperature and water. As a result different characteristic time ( $\tau$ ) were identified for the two stages of HT modification with values of 18 h for the first stage and 2600 h for the second one while for T modification only one stage was identified with a value of 7000 h. In addition, as indicates Table 2, the slope parameter of the second stage in HT modification was almost the same as for the T modification but at the same time was almost the double of the first stage. From these evidences, we could guess that in HT modification, compared to T modification, at least one supplementary chemical reaction was occurring which



**Figure 1:** Mass variation at oven dry state experimental data after (a) exposition to ventilated open air oven and (b) saturated steam in a laboratory scale autoclave.



**Figure 2:** Master curves identified on the experimental mass variation measured after time shifting to the reference temperature  $\theta_{\text{ref}} = 150\text{ }^{\circ}\text{C}$  for (a) the ventilated oven and (b) saturated steam heat treatment conditions.  $ML_{(-\infty)}$  is the dry mass loss at infinite time,  $ML_{(-\infty)}^1$  for the first stage and  $ML_{(-\infty)}^2$  for the second stage in saturated steam modification.

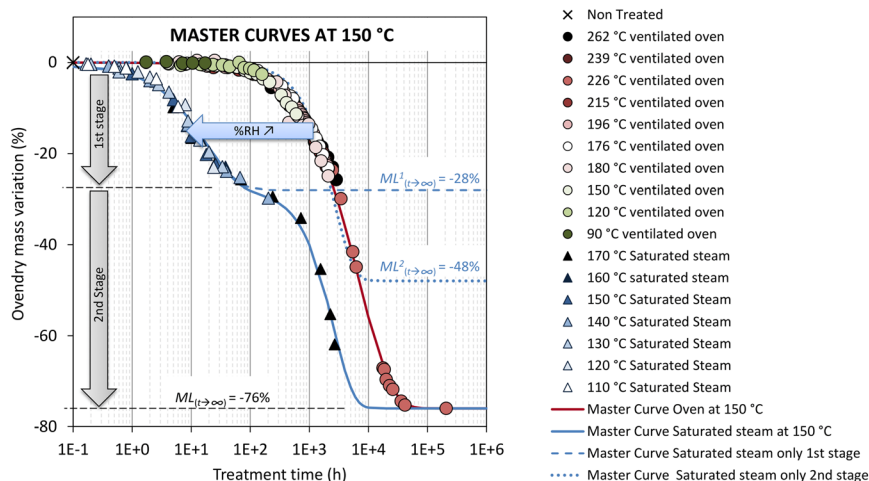
**Table 2:** Model parameters for the 2 wood modification processes.

Technology	1st stage				2nd stage (when present)				References
	$ML_{(t \rightarrow \infty)}$ (%)	$\tau$ (h)	$p$	Slope (%/log(h))	$ML_{(t \rightarrow \infty)}$ (%)	$\tau$ (h)	$p$	Slope (%/log(h))	
Ventilated oven	-76	7000	0.8	-46.5	/	/	/	/	Goli et al. (2014b); Marcon et al. (2018)
	$E_a^T = 112 \text{ kJ/mol}; A_{(T)}/A_{(T_{\text{ref}})} = 0.0064 \times T; \theta_{\text{ref}} = 150 \text{ }^\circ\text{C}; RH_{\text{ref}} = 0\%$								
Saturated steam	-28	18	0.8	-18.6	-48	2600	1.3	-46.0	
	$E_a^T = 118 \text{ kJ/mol}; A_{(T)}/A_{(T_{\text{ref}})} = 0.0065 \times T; \theta_{\text{ref}} = 150 \text{ }^\circ\text{C}; MC_{\text{ref}} = 0\%$								

degrades the cell wall at higher speed. The  $p$  parameter for T modification and for the first stage of HT modification were both equals to 0.8 while for the second stage of HT modification  $p$  was identified to be 1.3. To ease the understanding of HT modification, the saturated steam master curve was decomposed in the 2 stages and both contributions were plotted separately in Figure 2 as dashed lines (the master curve for HT modification is the sum of the 2 stages). This confirmed how the second stage (dashed blue line) of HT modification kinetic started to act at the same moment (almost equivalent  $\tau = 2600$  h) and with the same slope than for the ventilated oven treatment kinetic (red continuous line) since the two curves are nearly overlapped (as Table 2 confirms). It can then be concluded that the same mechanism of degradation was acting for both T treatment and the HT second stage treatment (after about 2600 h at  $150\text{ }^{\circ}\text{C}$ ), when the first stage of HT modification was almost ended. If only focussing on the mass variation,

the time efficiency of HT modification compared to T seemed to be entirely attributed to the first stage which stops at about 28% of mass loss. As the first stage ended the modification under dry or saturated steam media seemed not to present relevant differences. No existing research work investigated thermal modification until such important dry mass losses as the present work did (76%). Degradation kinetics experiments both for T and HT modifications were usually stopped beyond 20%  $ML$  because above this threshold the mechanical performances of the material are compromised, explaining why such conclusion was never brought before.

The models were compared to experimental data in Figure 3 where the master curves were shifted back to the relative real modification temperatures using the modified Arrhenius law and the respectively identified energy of activation. This comparison showed a good predictive accuracy of the model for both T and HT modification.



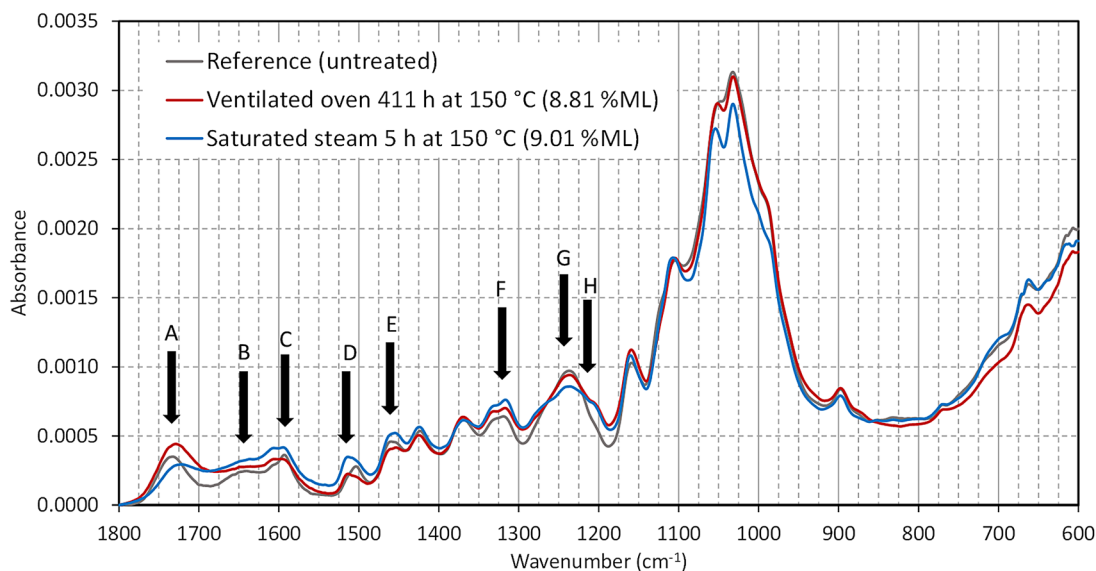
**Figure 3:** Dry mass loss kinetics predicted with the model vs. the experimental data for (a) ventilated oven and (b) saturated steam modification processes.  $E_a$  are the energies of activation identified for each thermal modification process resulting in a time shift toward the left (minor treatment duration) when the temperature ( $\theta$ ) increases.

The differences between dry and saturated steam heating were entirely interpreted by different chemical reactions driven by temperature and relative humidity. However, pressure-dependent activation energy in the case of saturated steam, as in Basile et al. (2014) considering a great variety of biomasses, could be an interesting complementary approach. Indeed, using partially saturated steam, each steam pressure can be obtained by different combinations of temperature and relative humidity. The data from the studies of Borrega and Kärenlampi (2008) on Norway spruce, Willems et al. (2015), and those of Altgen et al. (2016) on European beech confirmed that, in the 1st-stage degradation range (<30% *ML*) and temperature range below 200 °C, the mass loss value and its derivative are explicitly dependent on the steam pressure, over the entire steam

saturation range from dry to full saturation. Accordingly, the difference in the master curves at 150 °C (Figure 2) could be interpreted as the consequence of a pressure increase rather than the relative humidity one. The main interest of such view is that it leans on a thermodynamic quantity, the media pressure. The pressure dependency was not explored in the present study but will be considered for future works aiming to suggest a generalized model for hygrothermal wood modification kinetic modelling.

### 3.3 FT-IR analysis

In order to give a better understanding of the reactions driving the mass variation FT-IR analyses was conducted.



**Figure 4:** ATR FT-IR spectra of poplar samples: Before heat-treatment (grey line), after 411 h oven exposure at 150 °C with mass loss 8.81% (red line) and after 5 h steam exposure at 150 °C with mass loss 9.01% (blue line). The labels A to H indicate the major spectra variations explained in more details in Table 3.



**Table 3:** Summary of the band modified after oven and steam treatment.

Label	Wavenumber (cm <sup>-1</sup> )	Ventilated oven	Saturated steam	Attribution (related reference)
A	1745–1715	–	Decrease/shift	Hemicelluloses C=O (Gierlinger et al. 2008; Schwanninger et al. 2004; Tondi and Petutschnigg 2015)
B	1665–1630	Decrease	Decrease	Water absorbed (Emandi et al. 2011; Gierlinger et al. 2008; Schwanninger et al. 2004)
C	1600–1585	Decrease	Decrease	Lignin S>G (Schwanninger et al. 2004)
D	1520–1490	Shift	Shift	Lignin G>S (Åkerholm and Salmén 2003; Schwanninger et al. 2004)
E	1465–1440	Slight decrease	–	Mixed (Gierlinger et al. 2008; Schwanninger et al. 2004)
F	1325–1305	Slight increase	Increase	Cellulose (Gierlinger et al. 2008; Schwanninger et al. 2004)
G	1250–1225	–	Decrease	Hemicelluloses (Schwanninger et al. 2004)
H	1215–1200	Increase	Increase	Cellulose (Schwanninger et al. 2004)

The results of the FT-IR spectra investigation can be observed in Figure 4 where samples with the same mass loss of about 9% for both treatments, and the spectrum of the reference free of any treatment samples, were compared.

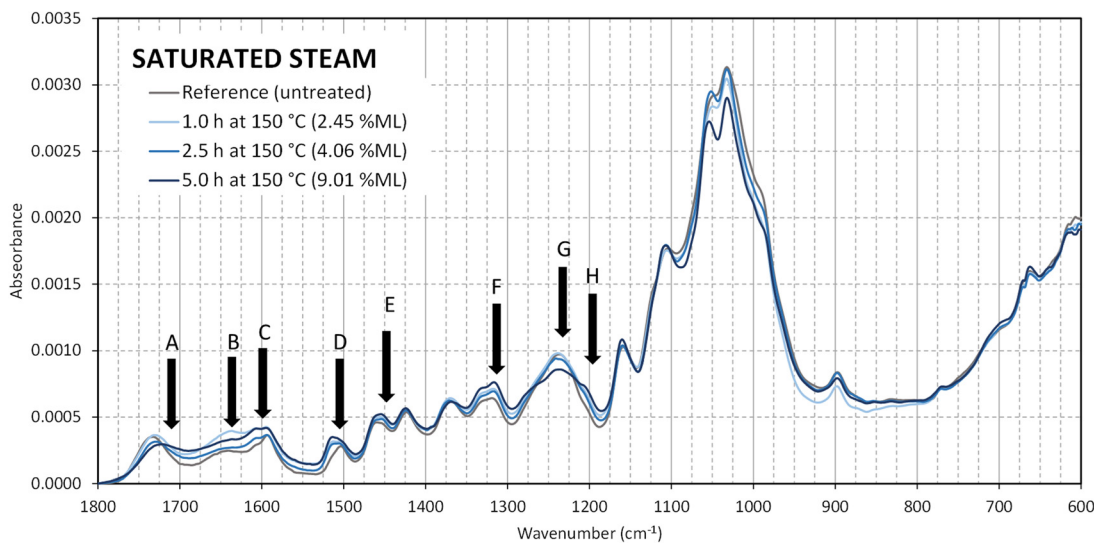
Ventilated oven and steam treatment presented significantly different profiles in the regions between 1800 and 1200 cm<sup>-1</sup>. In Table 3 the modified bands were described and attributed according to literature.

The signals attributed to lignin (C, D) were slightly decreasing for both treatments and in particular, the syringyl fraction decreased substantially, while the guaiacyl part shifted to higher wavenumbers. This could be attributed to the degradation process that affected principally the most substituted *p*-hydroxy cinnamic units, with release of methoxy-moieties. Conversely, the signals of hemicelluloses (A, G) decreased exclusively for the steam treated samples

meaning that the ventilated oven treatment did not affect hemicelluloses until 400 h exposure at 150 °C. The increase of the signal A of hemicellulose for the ventilated oven could be due to the fact that their relative amount was higher (due to the degradation of lignin). The other major differences could be attributed to the decrease of water affinity after both modifications (B) together with a relative increase of the cellulose bands (F, H). The band E could be attributed to different wood components and hence it was not possible to correlate it with the degradation process properly.

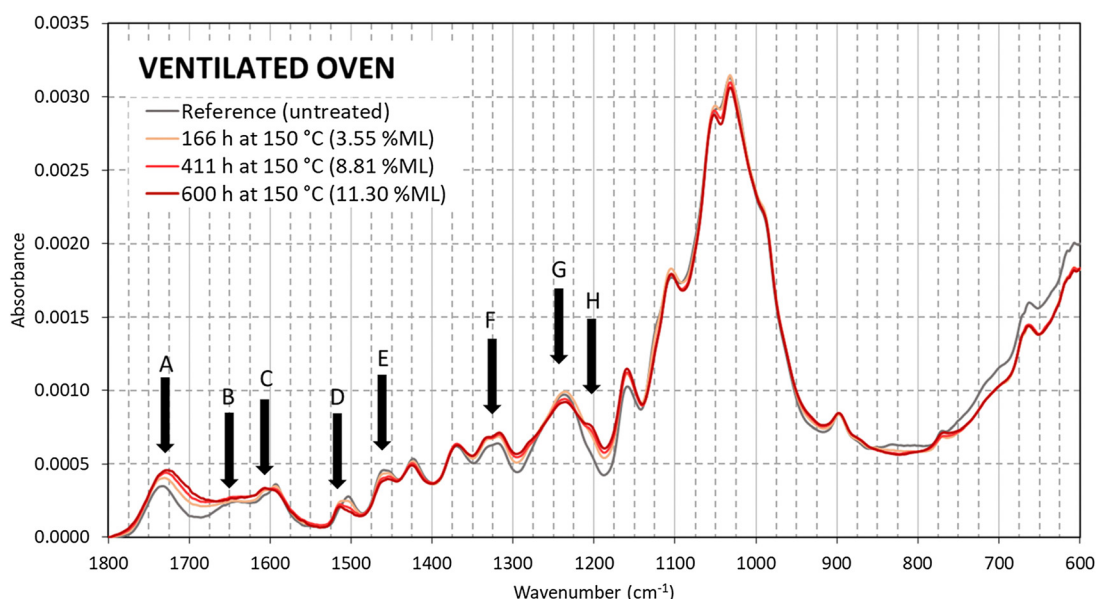
The steam process affected the lignin and the hemicelluloses to a different extent (Figure 5). The lignin started its degradation already after 1 h at 150 °C (C, D), while the hemicelluloses started to degrade after 2.5 h (A, G).

On the contrary, as displayed in Figure 6, the treatment in ventilated oven showed limited modifications also after



**Figure 5:** ATR FT-IR spectra of poplar samples exposed to saturated steam conditions at 150 °C: before modification (grey line), after 1 h (pale blue line), 2.5 h (blue line), and after 5 h of exposure to saturated steam (dark blue line). The labels A to H indicate the major spectra variations explained in more details in Table 3.





**Figure 6:** ATR FT-IR spectra of poplar samples exposed to ventilated oven conditions at 150 °C: before heat-treatment (grey line), 166 h (pale red line), 411 h (red line), and after 600 h of exposure (dark red line). The labels A to H indicate the major spectra variations explained in more details in Table 3.

600 h, however it can be seen that the degradation of lignin continues (C, D) while no/limited degradation of the hemicelluloses was observed (A, G).

To resume, under steam degradation, lignin begun its degradation immediately and slightly later, when the mass loss was around 4% the hemicelluloses were affected too. After 5 h, when degradation reached 9%, the hemicellulose part was significantly affected suggesting a faster degradation kinetic for this component. The treatment in ventilated oven showed a different degradation profile (Figure 6). The bands of lignin (C, D) had a similar trend observed also for the steam treatment, while the bands G of hemicelluloses appeared more stable. This suggested that without steam, hemicelluloses were more likely to resist the thermal degradation.

These observations confirmed the difference in the degradation kinetics: in dry conditions a “constant” degradation occurred, while under saturated steam, the hemicelluloses degraded much faster and this involved a “two-step” degradation kinetics.

## 4 Conclusions

This work showed how both thermal (T – ventilated oven starting from dry state) and hydro-thermal (HT – saturated steam starting from 12% MC) modification processes could be successfully modelled with the Arrhenius law and the time temperature superposition method. Master curves at

the reference temperature of 150 °C for both processes were computed up to a 76% of mass loss, a target of mass loss never reached before in this kind of studies. The two master curves have shown relevant differences both in terms of time shift and shape. In T modification master curve showed the usual shape already well known from literature, slowing down the rate of degradation when time increases up to a sub asymptotic behaviour. On the other side, the HT modification showed a two stage master curve with a higher degradation rate in the initial phase that slowed down when a mass loss of 28% is reached. The two stage master curve were split in two different master curves showing how the second stage of the degradation kinetic for HT modification presented a behaviour very similar to the T modification that was attributed mainly to the simple thermal degradation of polymers. The first stage of degradation kinetic for HT modification had a completely different behaviour in terms of master-curve descriptors highlighting a very different process that was supposed to depend on the presence of water. The FT-IR analysis confirmed these hypotheses showing how, for the T modification conditions, the main degradation acted on lignin while in HT modification the hemicelluloses were highly degraded since the beginning.

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